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Materials and methods for encapsulation of OPV: A review

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ABSTRACT

Amongst alternative energy sources, photovoltaics hold a considerable promise for it is a plentiful, easily accessible and renewable source of power. Yet, the overall cost of generating electricity using the most advanced silicon based solar cells remains high compared to both traditional and other renewable power generation approaches. Organic thin film photovoltaics are an emerging economically competitive photovoltaic technology that combines manufacturing adaptability, low-cost processing and a light-weight, flexible device end-product. At present, however, commercial use of organic photovoltaics is hindered by low conversion efficiency and poor overall stability of the devices. Encapsulation with high barrier performance materials and structures is one of the key ways to address these issues and improve device lifetime. This paper will briefly outline the current understanding of the major degradation mechanisms, their interrelation and the internal and external factors that initiate these processes. Then, the paper will provide an overview of currently available encapsulant materials, their utility in limiting chemical (water vapor and oxygen penetration) and mechanical degradation within individual layers and device as a whole, and potential drawbacks to their application in organic photovoltaic devices.

Contents

1. Introduction

In spite of slowing electricity growth in developed countries such as US and efficiency gains from new appliance standards and advances in power-efficient technologies, increasing urbanization and economic growth in countries such as China and India

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continues to drive worldwide demand for energy. Indeed, although the growth of US electricity demand has declined from a 9.8% annual rate of growth in 1949–1959 to only 0.7% per year in the first decade of the 21st century, China has recorded an annual average rate of 13% over the past decade. The need for energy is likely to expand even more in the coming years. According to U.S. Energy Information Administration Annual Energy Outlook 2013, in the US alone, total electricity demand is expected to grow by 28% over the next 30 years, from 3839 billion kilowatt hours in 2011 to 4930 billion kilowatt hours in 2040. To meet this energy demand, fossil fuel (oil, gas and coal) is currently the most widely used energy source, accounting for up to 70% of electricity produced globally. In China, electricity generation continues to be dominated by coal, at 80% of total power produced. Such high dependence on burning of natural resources raises significant concerns, in terms of both limited availability of fossil fuels and energy-associated emissions [1].

Growing environmental concerns, depleting natural resources, and associated price volatility of crude and refined oil have stimulated the demand for alternative energy sources. Amongst alternative energy sources, photovoltaics (PV) hold a considerable promise for it is a plentiful, easily accessible and renewable source of power, whereby solar radiation is directly converted to electricity. In addition to being abundant, solar radiation is also widely available geographically, giving photovoltaic technology a significant portability and scalability advantage over other alternative energy technologies, e.g. hydro and nuclear power generation. Overall, photovoltaics are regarded as an environmentally friendly and a non-pollutant low maintenance energy source [2]. In spite of significant recent advancements in the area of solar energy generation and declining prices for PV units, the overall cost of generating electricity using this method remains high compared to both traditional (fossil fuel based) and other renewable power generation (e.g. hydro) [3]. This holds true for even the most advanced solar cells. The primary contributor to the overall cost is expensive processing techniques involved in commercial solar cell manufacturing. At present, crystalline silicon (Si) cells remain the dominant PV technology, accounting for close to 90% of all commercially available PV products. Used for their high efficiency relative to other currently available PV technologies, solar cell manufacturing based on this technology is growing at approximately 40% per year and this rate of growth is still rising [4]. However, the fabrication of the simplest Si cell is a complex and expensive process that has to take place under controlled conditions, such as high vacuum and temperatures of up to 1400 °C. Concerns have also been raised regarding other materials used in PV devices, e.g. cadmium telluride (CdTe) and copper indium gallium selenide (CIGS). Among the most notable issues are those related to environment (e.g. toxicity of cadmium), price volatility (in particular with indium), and shortage of rare earth elements (e.g. tellurium) [5]. Finding an alternative PV technology is therefore essential and organic photovoltaics (OPV) have gained much attention in this regard during the past decade [5,6].

Organic thin film photovoltaics are an emerging economically competitive photovoltaic technology that combines manufacturing adaptability, low-cost processing and a lightweight, and flexible device end-product. The OPV technology is based on semiconducting polymers and small molecules, with significant implications to both PV device manufacturing and operations. The key property that makes OPV attractive is the potential to lower manufacturing costs by using reel-to-reel processing on low cost substrates, with numerous printing techniques, namely screen, inkjet, offset or flexo printing, already available [7]. In addition to printing, high throughput deposition processes such as physical vapor deposition (PVD), plasma enhanced chemical vapor deposition (PECVD) and other low temperature processes are widely used for fabrication of devices based on organic materials [5]. These processes typically require less energy compared to those employed for manufacturing of inorganic devices, thus lowering the overall device production budget [8]. Moreover, synthetic flexibility associated with the use of polymers allows for the design of organic materials with the desired properties, in terms of both operational performance and suitability for low-cost processing. For instance, precursor solubility in organic solvents is highly desirable, as it allows for low-cost large-scale coating and printing deposition methodologies to be used. The ability of these organic materials to be fabricated on a range of flexible, lightweight substrates has the potential to significantly enhance the application scope of PV technology, from stationary PV panels for household energy generation to portable power supply for small electronic devices. The potential to be transparent, ease of integration in different devices, and significant environmental advantages compared to traditional solutions (e.g. the smallest carbon footprint) are amongst many other attractive features of organic materials. Considering the aforementioned attractive features of OPV, there has been a growing interest in the technology from industry and research groups alike, as reflected through a number of high quality reviews and special issues with different degrees of specialization [2,7–39]. The reviews available generally focus on the polymer and organic solar cells [7–11], low band-gap materials [12,13] and small molecule solar cells [14].

Undoubtedly promising, currently available OPV technology is yet to reach a desirable level of performance, which would render it suitable for wide commercial use. Present power conversion efficiency (PCE) and operational stability of OPV are considerably lower than those offered by Si technology. Significant research efforts have been devoted to development of materials, designs and structures to improve PCE of OPV, with a recent report of 10.7% for a tandem cell [40]. Although this value falls short of 25–30% PCE level offered by Si PV cells, it may well be sufficient for a feasible commercial proposition when substantially less expensive production budget for OPV is considered. Long-term operation stability of OPV, however, is far below what would be considered acceptable for a commercial product, with the replacement costs negating the cost savings from inexpensive manufacturing. Currently, the acceptable lifetime of an inorganic solar cell is 20–25 years [41], well beyond the lifetime achievable by the most advanced organic solar cells currently available. Such profound discrepancy in device life expectancy between inorganic and organic PV cells stems from relatively high susceptibility of organic materials to water vapor and oxygen, which lead to reduced reliability and lifetime of organic devices under normal environmental conditions. As such, untimely degradation of individual materials and loss of device integrity are key limitations that hinder advancement and commercialization of OPV technology [41].

The past decade has seen the development of main mechanisms responsible for degradation of properties within the individual layers within polymeric OPV cell, from photoactive layer to electrode to interconnection to encapsulation. Grossiord et al. [3] reviewed our present understanding of the degradation mechanisms within OPV, highlighting the multi-trigger, multi-site and interrelated nature of these mechanisms and their synergistic effect on temporal decay in *I–V* curves. From their work and reports of others, it is evident that the overall stability of OPV cell is dependent on the stability of the actual photoactive component, the barrier and substrate layers and the interfacial stability. As such, significant research efforts have been directed towards increasing these stabilities, with most efforts concentrated on improving the intrinsic stability of photoactive materials within the cell structure [7,13,42–44]. Some of the approaches included use of photoactive layers with more stable monomer units and

minimal number of reactive side groups, stabilization through introduction of additives, optimization of polymer synthesis routes to minimize incidence and concentration of impurities, and post-synthesis purification treatments, to name but a few [3]. Another highly effective strategy to extend the device lifetime involves changes in the device architecture to inverted geometry.

Much work has been devoted into the development of superior quality encapsulation technologies to limit oxygen and moisture permeation from the environment into device layers. Suitably high barrier performance encapsulation materials and structures can further extend device stability and life expectancy providing sufficient durability to render OPV commercially attractive [45–48]. However, these materials have to meet the requirements of good processability, high optical transmission, high dielectric constant, low water absorptivity and permeability, high resistance to ultra-violet (UV) degradation and thermal oxidation, good adhesion, mechanical strength, and chemical inertness [49]. Due to the good combination of these properties and established history of acceptable durability, inorganic materials are most commonly used as encapsulants [50]. However, organic encapsulation materials offer significant advantages over inorganic counterparts, including flexibility in the synthesis of the organic molecules, which allows parameters such as the molecular weight, energy levels, bandgap and solubility to be altered [7]. They are also disposable and have lower negative impact on the environment [26]. Therefore, organic barrier materials may be more suited for the development of inexpensive all–organic PV cells [51–53].

It is the aim of this paper to review the literature relevant to different materials and techniques for encapsulation of OPV according to the present understanding of the efficiencies, advantages and reliability issues. This paper will briefly outline the current understanding of the major degradation mechanisms, their interrelation and the internal and external factors that initiate these processes. Then, the paper will provide an overview of currently available encapsulant materials, their utility in limiting chemical (water vapor and oxygen penetration) and mechanical degradation within individual layers and device as a whole, and potential drawbacks to their application in organic photovoltaic devices. A comparison between different materials is also presented here. While degradation studies using other technologies presented in this paper are very informative and similar to OPV, they may not be directly relevant to this technology.

2. Organic photovoltaics (OPV) – concept

OPV, a novel technology, is based on thin films of organic semiconducting polymers [3]. The ability to tailor the molecular properties to fit the application is an important advantage of these materials. The modules built are lighter and more flexible compared to their heavy and rigid inorganic counterparts, and thus less prone to damage and failure [2]. Moreover, semiconducting polymers combine the opto-electronic properties of conventional semiconductors with the excellent mechanical and processing properties of polymeric materials [2]. These can be processed from solution at room temperature onto flexible substrates using simple and therefore cheaper deposition methods [7]. As a result, considerably less effort and production energy is needed. In addition, OPV shows other advantages including low material requirements and the utilization of eco-friendly materials [2].

Energy conversion efficiencies achieved to date using organic polymers are low compared to inorganic materials. However, OPVs have improved quickly in the past decade and recent progress achieved using organic mono-crystalline, multilayered thin films and interpenetrated network technologies show the potential of a very fast increase in the conversion yield of OPVs [39,40,53–56].

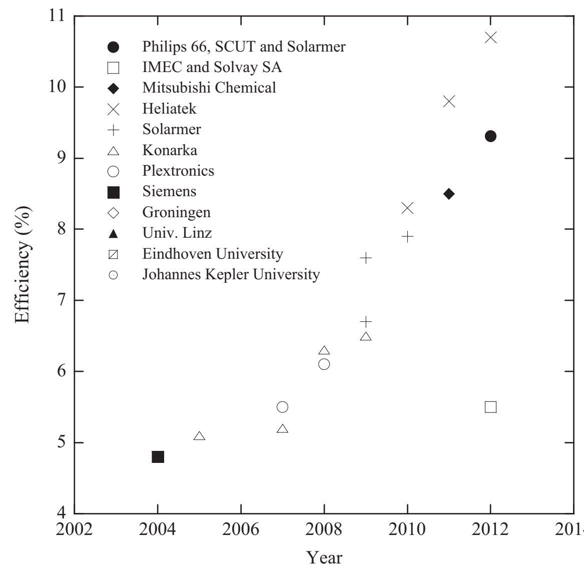


Fig. 1. Advancement of the maximum OPV cell efficiency.
Source: Solarmer Energy Inc.

External quantum efficiencies (EQE) have been increased by 50% using the bulk heterojunction structure [57] and 80% EQE is reported for blends of conjugated polymers with fullerenes [58]. The conversion efficiency of organic photovoltaic (OPV) solar cells has significantly increased over the past decade as depicted in Fig. 1 [40].

3. Reliability issues of OPV

Organic materials are by nature more susceptible to degradation from oxygen and water than inorganic materials. A number of studies have been carried out and they show that the stability/degradation issue is quite complicated and not yet fully understood, though progress has been made [3,21,59–61].

Chemical degradation of organic solar cells mainly focuses on the role of oxygen, water and electrode material reactions with the active polymer layer [3]. Oxygen is readily activated by UV illumination in the presence of sensitizers such as titanium oxide or other organic molecules [59]. The superoxide or hydrogen peroxide formed may then forcefully attack any organic substance present including the active polymers. Some materials are more vulnerable to degradation than others, e.g. oxygen and water can diffuse into the device through a simple layer of poly[[[(2-ethylhexyl)oxy]methoxy-1,4-phenylene]-1,2-ethenediyl] i.e. MEH-PPV sandwiched between indium tin oxide (ITO) and aluminum (Al) electrodes [62]. This diffusion through thin films is addressed elsewhere [63–70]. Furthermore, diffusion through outer electrode proceeds via microscopic pinholes present [59]. Metal grains that evaporated electrodes typically consist of are other possible diffusion channels. Swelling is observed on the outer electrode surface centered on the microscopic pinholes in the electrode surface due to the oxidization and expansion of the organic material in all directions [69]. This degradation of the electrodes generally leads to the degradation of the photoactive layer (PAL)–electrode interface due to a decrease of the interfacial area because of formation of insulating patches and/or voids [3]. All these changes deteriorate the charge transfer between the PAL and electrodes, which can be coupled to mechanical breakdown and ultimately to delamination when longer exposure times and/or mechanical stresses are considered [21,71–75]. Alternatively, insulating patches can also be created by other chemical reactions

between the PAL and the metal electrode. As an example, radical species formed in the PAL may react with the aluminum (Al) electrode, leading to a gradual degradation of the PAL–electrode interface quality [76].

The mechanical properties of various polymers with high device PCE have been studied [3,49,59,60,69,72,73,77,78]. An important parameter for the quality of these polymer films is their resistance to mechanical damage. However, scratch resistant polymer films very often cause embrittlement of the system [79]. The decrease of molar mass resulting from chain scission process is responsible for this [80]. Chain scission also induces chemicrystallization. These two processes can lead to embrittlement through two possible causal chains: (1) chain scission→molar mass decrease→chemicrystallization→decrease of the interlamellar spacing→embrittlement; and (2) chain scission→molar mass decrease→chemicrystallization→decrease of the tie-macromolecule concentration→embrittlement [80]. This may also result in modification of the optical properties of the polymer (i.e. decrease of transparency), as well as an increase of light scattering due to physical reorganization of the polymer chains [3]. Samples fabricated from poly(methylmethacrylate) (brittle layer) and polycarbonate (substrate) as well as from styrene–acrylonitrile and acrylonitrile–butadiene–styrene copolymers show this phenomenon [81]. Furthermore, if the system is stressed, cracks can be initiated in the film, and trigger fracture in the polymeric substrate due to the stress intensity at the crack tip [69].

In addition to the degradation mechanisms listed above, electrical output of PV module can be significantly affected by various factors such as moisture, UV light, temperature etc. [82]. Exposure to oxygen has been found to lower the conductivity of thin films. Upon oxygen uptake, the electron mobility is reduced by several orders of magnitude because the introduced oxygen acts as an electron trap [83]. The permeability of polymers is influenced by both the mobility of the polymer chains and the strength of the interaction between the polymer and penetrant. Moreover, chain scission increases the free volume of the polymer system, which can lead to an increase in permeability and decrease in mobility [59]. This reaction also affects the ordering of the polymer chains that contributes to cell degradation as they affect charge transport. As a result, short circuit current density, J_{sc} decreases, which induces a drop of the OPV cell efficiency [3].

Optical properties of polymers typically are not influenced by changes in temperature or the application of stress [59]. However, simultaneous application of stress and temperature can induce crystallization and the growth of spherulitic structures that scatter light and decrease clarity. Chain scission reactions can lead to the formation of chromophores that may drastically increase absorption in either the UV or visible spectral range or both [3].

Soil accumulation is another issue that reduces light transmission of the solar cells and therefore, reduces power output [49]. Presence of dust particles in the stacking or the organic PAL layer–electrode interface can induce higher local electrical fields, paving the way to the formation of microscopic conduction paths through the organic layer during operation [84].

The reliability issues discussed above should be solved to maintain stability and lifetime of OPV. Encapsulation can be a solution to these issues [85]. The desired encapsulation method may block oxygen and water effectively which in turn provides a solution to the diffusion through microscopic pinholes [48]. This also prevents insulating patches and/or voids and therefore, photoactive layer (PAL)–electrode interface remains stable. As a result, charge transfer between the PAL and electrodes does not deteriorate. Encapsulation also provides resistance to mechanical damage and structural support. It can absorb the stress that prevents cracks to be initiated and fractures to be triggered. Encapsulation offers optical coupling, electrical isolation, physical isolation and thermal conduction for the solar cell assembly that keeps the electrical output and the optical properties stable for the desired lifetime [86]. It should be thin and lightweight to take full advantage of the potentials of OPV cells in practical applications [86]. However, the currently available materials do not satisfy all of these issues [87].

4. Encapsulation requirements

Due to the young age and rapidly evolving nature of the OPV technology, as well as complex mechanism of OPV device degradation, the encapsulation requirements for OPVs are not fully defined even though the ongoing research efforts are devoted to determine these. However, some important aspects of encapsulants are high dielectric breakdown, high volume resistivity and matching refractive index (n) with other layers. Water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) are the steady state rates at which water vapor and oxygen (respectively) gas can penetrate through a film that affects the encapsulation layer. Another important material property often discussed in encapsulation is the glass transition temperature (T_g), which is a function of chain flexibility. The glass transition occurs when there is enough vibrational (thermal) energy in the system to create sufficient free-volume to permit sequences of 6–10 main-chain carbons to move together as a unit. At this point, the mechanical behavior of the polymer changes from rigid and brittle to tough and leathery (plastic behavior). In case of temperature extremes, it is important to know what the potential exposure temperatures are and how they will affect the mechanical behavior of the material. Moreover, measurement of light transmission is important for encapsulation due to the need for transparent materials. Hydrolysis, UV absorption degradation and some other aspects are also important to define the encapsulation requirements. A list of these requirements and specifications is given in Table 1 [49].

5. Thin film encapsulation

The relatively strong sensitivity of OPV devices to water vapor and oxygen, which induces degradation, places stringent demands on the barrier performance of encapsulation materials and structures. To meet these encapsulation requirements, different approaches have been adopted such as single layer and multilayer encapsulation.

5.1. Single layer thin film encapsulation

Single layer thin films are attractive because of the simplicity of the manufacturing process compared to multilayer thin film encapsulation methods that require multiple processing steps. Inorganic single layer encapsulating films are limited in their performance mainly due to the existence of defects in the films, which provide pathways for water vapor and oxygen to permeate through the barrier layers [88]. In fact, research into developing single layer encapsulation films has mainly focused on the reduction of these defects to improve barrier performance and organic films can address this issue effectively [89].

5.1.1. Inorganic materials

5.1.1.1. Silicon (S_i). Thin films of Si are noted to be suitable for encapsulating solar cells [47,90]. This is primarily due to its high transparency in the UV–visible wavelengths, excellent tolerance to high optical flux and excellent thermal and environmental stability [90]. Depending upon the chemical constituents

Table 1
Specifications and requirements for encapsulant materials.

Characteristics	Specification or requirement
WVTR	10^{-4}–10^{-6} g m^{-2} day^{-1}
OTR	10^{-3}–10^{-5} cm^3 m^{-2} day^{-1} atm^{-1}
Glass transition temperature (T_g)	<-40 °C (during winter in deserts)
Total hemispherical light transmission over the wavelength range from 400 nm to 1100 nm	$>$ 90% of incident light
Hydrolysis	None (80 °C, 100% RH)
Water absorption	$<$ 0.5 wt% (20 °C/100% RH)
Resistance to thermal oxidation	Stable (up to 85 °C)
Mechanical creep	None (90 °C)
Tensile modulus	$<$ 20.7 MPa ($<$ 3000 psi) at 25 °C
Chemical inertness	No reaction (with embedded Cu coupons at 90 °C)
UV absorption degradation	None ($>$ 350 nm)
Hazing or clouding	None (80 °C, 100% RH)

attached to the atom, Si can be formulated to a wide range of refractive indices (between 1.38 and 1.58) [91]. Due to its low modulus and low glass transition temperature (–50 °C), Si is stress relieving over a wide temperature range. It is well known as a dielectric insulator and has high volume resistivity [88]. Moreover, because of hydrophobicity, it has low moisture pick-up in damp-heat environment and in total water immersion [92]. Damp-heat has a negative influence on devices [82,93], e.g. CIGS cells suffer from reduced open circuit voltage (V_{OC}) and fill factor (FF) [94]. Low moisture of Si uptake is therefore an excellent property for its use as an encapsulant [90].

5.1.1.2. Silicon nitride (SiN_x). SiN_x thin films can be deposited using radio frequency (RF) PECVD and low frequency (LF) PECVD. However, films deposited using these processes show significant differences. The layers deposited with LF PECVD show lower values of extinction coefficient for the same refractive index values, which means that LF PECVD layers have lower absorption and are more suitable for PV [95]. Fourier transform infrared spectroscopy (FTIR) characterization shows that LF PECVD layers have the highest Si–N bond density at 1.2×10^{23} cm^{-3} [95]. The maximal density of the film deposited by LF PECVD at 360 °C is equal 2.6 g/cm^3, which is lower than the value (2.8–3 g/cm^3) required to obtain high efficiency [95]. An efficiency of 14.1% was found with V_{OC}=590 mV at 360 °C for solar cells with SiN_x layer deposited by LF PECVD. The OTR and WVTR for SiN_x films are below the detection limit of MOCON method (0.01 cm^3 m^{-2} day^{-1} and 0.01 g m^{-2} day^{-1}, respectively) [96]. Low stress for these films is also important for encapsulation purpose [97].

The reason for middling behavior of the SiN_x film deposited by RF PECVD may be due to the extent to which the chemical structure of the polymer differs from that of the monomer and the power level used during the deposition. The degree of monomer fragmentation is determined to a large extent by the intensity of the plasma field, with the higher bond dissociation corresponding to the increased magnitude of the RF energy input [98]. Furthermore, there is an increase in the temperature of the substrate associated with higher applied power. Lowering the substrate temperature encourages condensation and adsorption of non-excited gaseous species and subsequent incorporation of an increased number of non-fragmented molecules or slightly fragmented precursors in the growth region of the film [99]. This process of integration of large fragments is driven by the reactive species, which arises as a result of plasma field. In addition, in agreement with a competitive ablation–polymerization concept [100], the respective rates for ablation and polymerization may have differing temperature dependencies and therefore it is possible that lower temperatures may result in a reduction of energetic particle damage [101]. Hence, by choosing appropriate RF power conditions, encapsulation films with material properties tailored to the desired application can be manufactured.

5.1.1.3. Aluminum oxide (Al_2O_3). Atomic layer deposition (ALD) is a promising alternative to PECVD. Encapsulation films have been achieved using Al_2O_3 [102,103] and Al_2O_3/HfO_2 nanolaminates [104] deposited by this process. H_2O is used as the oxidant in both approaches. However, the films deposited by ALD using H_2O as the oxidant have a high impurity content, particularly of hydrogen [105]. A longer time is also needed during deposition to purge water molecules from the surface of the cell, as water has a high surface affinity owing to its large dipole moment [105,106]. This problem reduces throughput of the process [107]. In current semiconductor technology, O_3 is the preferred oxidant and higher throughput is gained from O_3-based ALD as the time required for surface reactions and purging of the unreacted surface adsorbed species is much shorter than H_2O-based processes [105–108]. This is due to the high chemical reactivity between trimethylaluminum (TMA) and O_3, meaning that it can be purged more efficiently than H_2O [108]. An O_3–Al_2O_3 film also shows smaller residual hydrogen concentration compared to H_2O–Al_2O_3 films [85,105]. Only Al_2O_3 is used as the primary barrier layer and no UV-curable epoxy resin film is used as an additional sealant for protecting OPVs from ambient moisture or oxygen. A WVTR of 1.7×10^{-5} g m^{-2} day^{-1} at 38 °C is found by quantitative Ca test [103].

The encapsulating ability of Al_2O_3 deposited using both O_3 and H_2O increases with increase in thickness, which is expected [85]. The efficiency of O_3-based ALD for device encapsulation is further highlighted by the fact that 10.2 nm of O_3–Al_2O_3 (120 cycles) offers better encapsulation than 20 nm of H_2O–Al_2O_3 (210 cycles) [85]. A thick film of 200 nm is used for the protection of OPV from ambient conditions and Al_2O_3 layer is deposited using H_2O at a growth rate of 10 nm/h [109]. However, 60% degradation is reported in device efficiency within 100 h, indicating extremely poor encapsulation by the Al_2O_3 layer grown using H_2O. In comparison, a device capped with 18 nm of O_3–Al_2O_3 shows 80% retention of the initial efficiency in over 500 h [109]. ALD also serves as the annealing step and irrespective of the anneal temperature, the O_3–Al_2O_3 layers showed superior encapsulation compared to the H_2O–Al_2O_3 film. Encapsulation by Al_2O_3 deposited using ALD is further demonstrated by the performance of pentacene/C_{60}-based OPV cells. These cells are found to be stable for 6000 h in ambient conditions with negligible deterioration in properties [109]. ALD encapsulation process on a pentacene/C_{60}-based PV device was performed at 100 °C and no negative impact on the device performance was observed, other than changes due to the effect of thermal annealing, which have been reported previously [110].

5.1.2. Organic materials

5.1.2.1. Ethylene vinyl acetate (EVA). EVA, a copolymer of ethylene and vinyl acetate, is one of the most widely used encapsulating materials among the single layer encapsulation films available [111]. It offers weather resistance and long-term reliability under long periods of exposure to different elements [112]. EVA has transmission of 91%, a volume resistivity of 0.2–1.4 10^{16} Ω cm and an adhesion strength of 9–12 N/mm (90° peel). Other advantages are its low cost, dimensional stability and volumetric fill. Therefore, based on the film extrudability and transparency, EVA was used for encapsulation purpose [113].

5.1.2.2. Europium doped EVA. EVA doped with a single europium (Eu^{3+}) complex whose sensitized region is broadened due to the

presence of a co-ligand 4,4′ bis(diethylamino) benzophenone (EABP), has been characterized optically and electrically for encapsulation purpose [114]. The Eu^{3+} complex shows an absorption band at 310 nm with full width at half maximum (FWHM) of 46 nm, while the EABP spectrum is centered at 360 nm with a FWHM of about 45 nm. Therefore, neither the organolanthanide complex nor the ketone is able to absorb visible light. But, a ground-state complex formed by EABP and tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) ($Eu(tfc)_3$) by the interaction of the positively charged Eu^{3+} ion with the electron rich carbonyl group can absorb visible light [114].

Coordinating EABP via its carbonyl group to the lanthanide ion gives rise to stabilization of the very polar energy levels involved. Therefore, doping the PV module encapsulating matrix with $Eu(tfc)_3$–EABP allows the exploitation of a wide portion of the solar spectrum. Moreover, europium doped EVA layers are able to induce down-shifting of photons with wavelengths lower than 460 nm. A 2.9% relative increase of the total power delivered has been observed [114].

5.1.2.3. Ethylene methyl acrylate (EMA). EMA, a copolymer of ethylene and methyl acrylate, has a potential advantage over EVA because it does not soften to a viscous melt above 70 °C and, may not need curing as does EVA to achieve high temperature creep resistance [49]. The key benefits of EMA are its thermal stability, adherence to various substrates, chemical resistance and good mechanical behavior at low temperature [49]. These qualities match with some of the requirements of OPV and therefore used for encapsulation purpose [115].

5.1.2.4. Polyvinyl butyral (PVB). PVB can be used as encapsulation layer which is already widely applied in modern mass production of thin film solar cells [44]. Where EVA is an elastomeric cross-linking material activated by exposure to heat and/or UV light, PVB is a thermoplastic product that is non-cross-linking on exposure to heat. As a result, PVB can retain its original chemical composition [116]. The advantages of the film fabricated from PVB are its optical transparency, adhesive properties on glass, solar cells, and other plastics, high bond durability, resistance to heat, UV light and environmental influences and high compatibility with module components [116]. It can strongly reduce the moisture permeation and degradation of CIGS-based solar cell and consequently ensure longer lifetime [117].

5.1.2.5. Thermoplastic polyurethane (TPU). Platilon® hot-melt adhesive films have been made of TPU to avoid the problem of time-consuming vacuum lamination. This film is superior to EVA due to the flexibility in bonding with relatively hard materials [118]. TPU films facilitate continuous, vacuum-free processing without cross-linking and emissions. These advantages scale up the productivity in the manufacture of OPV devices. It shows much less UV-induced yellowing and bonds better to substrate than EVA [119]. Several companies such as SunWare Solartechnik GmbH, Bemis Worldwide etc have introduced TPU encapsulation films, which show improvements over non-encapsulated devices [119].

5.1.2.6. Cyclized perfluoropolymer (Cytop™). For creating commercially viable encapsulation structures for flexible OPV devices, a commercial polymer Cytop™ was reported [120]. This polymer is transparent, amorphous, and can be deposited using conventional thin film deposition techniques such as spin coating. It is available as a high viscosity resin with chemical structure shown in Fig. 2. Atomic force microscopy (AFM) analysis shows that spin coating of this resin yields very smooth films with a root mean square roughness of 3.8 Å [120]. Contact angle analysis

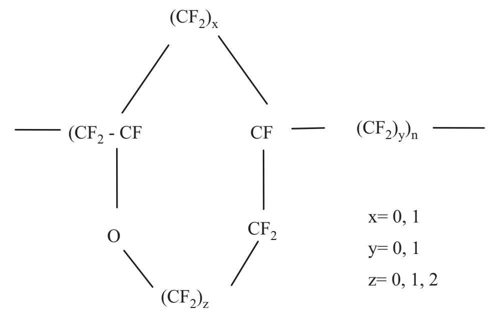


Fig. 2. Chemical structure for Cytop™ [121].

defines the material as hydrophobic having a water contact angle of 110°. This material provides a good oxygen/water-vapor barrier in lifetime tests of organic light emitting diodes (OLEDs) [121]. OLED's are even more sensitive to oxygen/water-vapor degradation than OPV. Cytop™ may therefore provide part of the barrier needed for commercially viable, flexible, printable solar cells [120].

5.1.3. Organic–inorganic hybrid materials

5.1.3.1. ORMOCER®(ORM). By using a technology combining organic and inorganic components through the sol–gel method, the organically modified ceramics or ORM is formed [122]. The main characteristic of this type of material is the incorporation of organic groups linked to the inorganic backbone formed by hydrolysis and condensation of alkoxides [123]. The combination of organic and inorganic networks in the ORM can enhance and improve resistance to chemical degradation [124]. Fraunhofer ISC (a materials research institute) introduced thin film based on ORM for encapsulation purpose, whose property profile can be varied almost at liberty with the aid of chemical nanotechnology [125].

All transparent materials reflect a certain amount of incident light. Surface structures in the submicron range can help to significantly reduce reflections by producing a smooth change in the refractive index at the surface boundary between air and the substrate. Structured ORM coatings typically reduce the reflection of a glass pane from 8% to 1%, thus increasing the transmission from 92% to 98% [125]. It has scratch resistance at layer thicknesses of only a few micrometers. It is highly transparent and has some other characteristics such as anti-soiling, antistatic or diffusion-inhibiting properties. OTR is measured below 0.01 $cm^3\ m^{-2}\ day^{-1}$ while the WVTR reaches the value of 0.01 $g\ m^{-2}\ day^{-1}$. These results are in the range of the necessary barrier requirements for the encapsulation of solar cells [125].

5.1.3.2. ORMOSIL aerogel thin film. In nature, many plants and animals utilize superhydrophobic surfaces with a water contact angle (CA) larger than 150° and a sliding angle (SA) lower than 10° [126–128]. Inspired by this structure, many artificial superhydrophobic surfaces have been produced with a variety of techniques [129–135]. However, simple, low-cost, and large area fabrication of superhydrophobic surfaces, vital for practical applications, is rarely achieved and with a view to achieving this goal, several surfaces have been introduced recently [136–139]. Highly transparent and organically modified silica (ORMOSIL) aerogel thin film is one of them that has good thermal and mechanical stability [136]. ORMOSIL materials show some unique properties, such as flexibility and stability at atmospheric conditions, which cannot be afforded by either organic polymers or glasses alone. Both chemical and physical properties of the resulting surfaces, such as wettability, can be changed by modifying the organic group on the ORMOSIL [140]. Moreover,

ORMOSIL aerogel thin films are highly transparent, do not need any pre- or post-surface treatments and can be applied on a variety of substrates at ambient conditions with common thin film deposition methods [136].

RMOSIL aerogel films have highly porous networks (Fig. 3) that provide high chemical and thermal stabilities, superior aging behavior and can facilitate a very short diffusion pathway for ions. These aerogel thin films contain both micrometer and nanometer scale roughness which provide superhydrophobicity. The films preserve their superhydrophobicity even after annealing at 500 °C for 1 h and also exhibit very high contact angle of 179.9° [136]. For higher temperatures, the contact angle starts to decrease and superhydrophilic films with contact angle less than 5° are obtained at 600 °C (Fig. 3d). The increase in the macroporosity results in higher static contact angle values. This increase stems from increasing roughness which allows more air to be trapped between the water and the surface [136].

Superhydrophobic coatings must be transparent to be used in OPV cells. However, high surface roughness required for superhydrophobicity lowers the transparency by scattering light [118,141]. ORMOSIL aerogel thin films are found to have an average surface roughness smaller than 100 nm, resulting in a highly transparent appearance. As a result, this approach is a suitable option for encapsulation of OPV [136].

5.1.3.3. Other organic materials. The air and encapsulation induced degradations affect the efficiency of organic thin film transistors (OTFT) and solar cells. To counteract the encapsulation-induced degradations in OTFT, ten types of encapsulating polymers over poly(3-hexylthiophene) (P3HT) are studied [142]. This research on OTFT gives us ideas about the degradation mechanisms and new encapsulation approach that can be applied on OPV. It is found that degradations could be avoided with polymers containing low-polarity functional groups, having poly(vinyl methyl ketone), poly(methyl vinyl ether), poly(methyl methacrylate), and polystyrene. Encapsulating polymers were poly(vinyl methyl ketone) (PVMK), poly(methyl vinyl ether) (PMVE), poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(vinylidene chloride-co-vinyl chloride) (PVDC-co-PVC), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVDF), polyacrylonitride (PAN), poly(vinyl alcohol) (PVA) and poly(vinyl phenol) (PVP). Of the 10 polymers tested, six polymers, namely PVA, PVP, PAN, PVC, PVDC-co-PVC, and PVDF induced strong p-type doping, i.e., they increased the off current (by 2–4 orders of magnitude), increased the on current (by 2–7 fold), and reduced the on/off ratio (by ~3 orders of magnitude). As a result, the P3HT layer encapsulated with the six doping-inducing polymers essentially becomes conductive, with conductivity rising from the pristine value of 1.1×10^{-5} S/cm to up to 1.6 S/cm [142]. The strong p-type doping by the six polymers was attributable to their electron-withdrawing functional groups. On the other hand, other 4 polymers – PVMK, PMVE, PMMA, and PS did not cause observable degradation [142]. This indicates that the functional groups on these polymers were not inducing charge–displacing interactions with P3HT. This was attributed to the lack of electron-withdrawing group on PS and PMVE [107]. On PVMK and PMMA, although there were the electron withdrawing carbonyl groups, the absence of degradation suggested that the interactions between P3HT and the carbonyl groups may have been hindered by the alkyl groups adjacent to the carbonyl groups [142].

Taking into account the identified sources of degradation, an encapsulation approach is demonstrated [142] which involves using a low-polarity encapsulating polymer (polystyrene) layer to serve as a moisture barrier and to avoid encapsulation-induced degradation. It also includes applying a light-blocking dye to eliminate the effects of oxygen [142]. This approach shows nearly constant device characteristics for >5500 h of storage in the ambient air. This long-term stability is a significant improvement over previously reported results [143–146].

5.1.4. Comparison among single layer encapsulation films

High transparency is found for Si polymers in the UV–visible band [90]. High transparency is found down to 250 nm compared to the cutoff of 400 nm for EVA. It requires no additional additives to protect against UV degradation such as those used in other encapsulants like EVA formulations [90]. However, Si is very permeable to gas and water vapor and damp heat caused reduction in transmission [92].

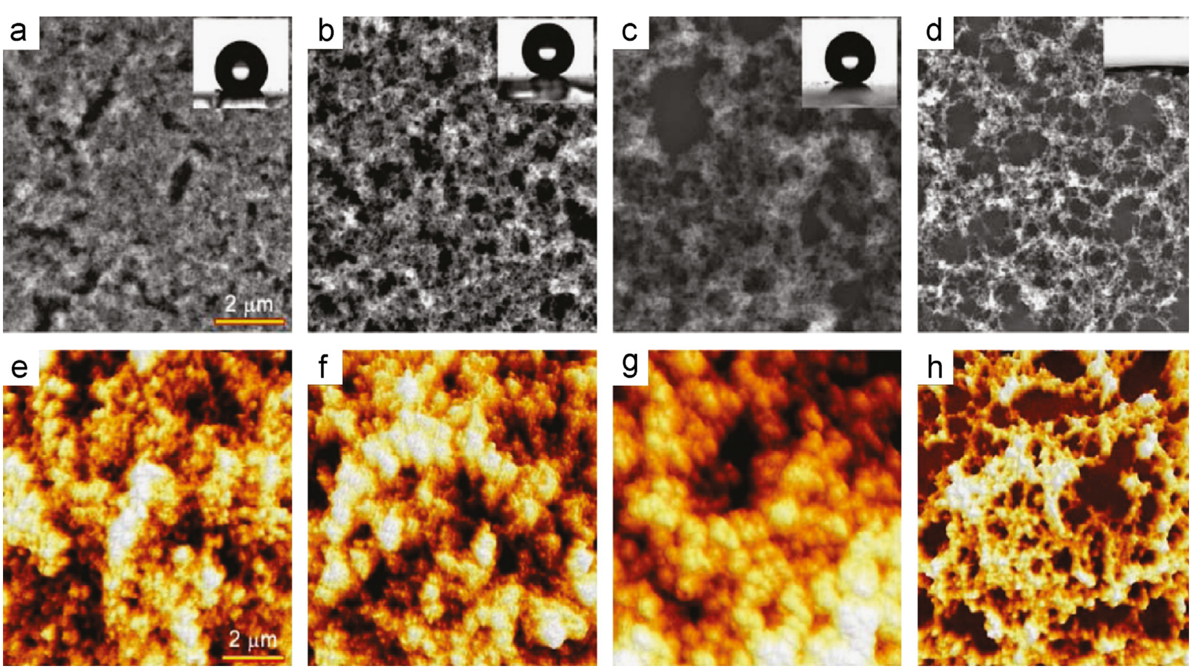


Fig. 3. Surface morphologies of ORMOSIL aerogel films [136].

Weatherability testing of EVA under UV irradiation and evaluation by FTIR measurements (Fig. 4) [112] shows apparent absorption growth at about 1715 cm^{-1} and 1175 cm^{-1}, both representing carbonyl C=O stretching vibration in the rapidly forming ketone structure [147]. Such ketone structures are unstable that can lead to molecular decomposition in EVA [112]. Furthermore, adhesion strength can be affected by the processing conditions, damp heat and exposure time.

Yellow browning is another problem with the EVA films which leads to large transmission (%T) loss and power loss [111]. Furthermore, EVA softens to a viscous melt above 70 °C and, therefore, must be cured (cross-linked) for service temperatures above 70 °C [49].

Improvements were monitored for SiO_x and SiN_x encapsulation films over non-encapsulated devices [96]. However, the deposition of the encapsulation structure may cause plasma damage on the devices owing to the high sensitivity of the organic films to radiation, charging and heating [148,149]. Introducing a buffer layer between the active layer and the barrier structure for reducing the plasma damage is therefore essential [78]. Encapsulation performance of Al_2O_3 is also found to be excellent [104,109]. However, their relatively slow deposition rate compared to PECVD-based methods makes them more difficult to use in low-cost mass manufacturing processes. EMA and PVB have the same problem as vacuum-bag lamination is needed for the fabrication that is a slow process [49,116].

5.2. Multilayer thin film encapsulation

Multilayer films are widely used for encapsulation of OPV devices and often consist of alternating organic and/or inorganic layers [45,46,48,50,107,150,151]. Examples of multilayer films include alternating layers of inorganic materials such as SiN_x and SiO_x deposited by PECVD or a combination of Al_2O_3/SiO_x deposited by ALD [107,152]. This multilayer approach is developed to thwart the defect issues limiting the barrier performance of single-layer encapsulation films. Defects which span the entire thickness of the individual inorganic layers are interrupted by applying multilayer films with alternating materials and do not channel continuously through the encapsulation film structure. This structure creates a path resulting in long effective diffusion pathways, increasing the barrier performance [153].

5.2.1. Inorganic materials

5.2.1.1. Silicon oxide (SiO_x) and silicon nitride (SiN_x). A barrier structure consisting of SiO_x and SiN_x films deposited via PECVD has been tested for the encapsulation purpose [152]. The WVTR of the barrier structure is ~3.12×10^{-6} g m^{-2} day^{-1} measured by a calcium test at 25 °C, 40% RH. This encapsulation structure shows less reactivity to water vapor and oxygen than individual SiO_x or SiN_x film [152]. Devices using the encapsulation structure are found to have a relatively low short circuit current density (J_{SC}) of 6.1 mA/cm^2, FF of 32% and PCE of 0.98% compared to the devices without barrier structure (J_{SC}=8.2 mA/cm^2, FF=37% and PCE=1.57%). This performance presents a high potential for the structure to be used for encapsulation purpose of OPV [152].

5.2.1.2. Nitrogen gas-phase spacer. Permeation of gases through polymeric barriers is frequently described by the "solution-diffusion" model [154,155], in which gas molecules dissolve in the barrier and then diffuse down a concentration gradient through the barrier. The total permeation rate is influenced by both the diffusion and the sorption properties of the permeant in the barrier. At steady state, the permeation rate is inversely proportional to the barrier thickness. However, increasing the barrier thickness increases encapsulation cost and to find an alternative encapsulation architecture that increases device lifetime without additional cost, contaminant-free (e.g. pure N_2) gas-phase spacers were inserted between free-standing barrier films in a multilayer structure (Fig. 5(a)) [156]. The nitrogen spacers act as sinks for permeating H_2O and O_2, delaying establishment of steady-state chemical potential gradients across the downstream barrier layers during the transient regime and thereby reducing permeation rates.

A limitation for the barrier performance of the encapsulation architecture (Fig. 5(a)) is the epoxy (E_1), attaching Barrier (1) to the glass substrate, through which contaminants can diffuse and reach the encapsulated device without ever passing through the high performance barrier material [157]. Although the exposed area (and hence the contaminants flux) of E1 is much smaller than Barrier (1), inexpensive epoxies are not optimized for barrier performance and so may have substantially higher permeabilities. As a result, diffusion through the epoxy may be large enough to result in significant flux of permeants through E1 [157]. This flux may constitute the limiting factor for encapsulation performance. Using an encapsulation architecture that minimizes transport through epoxy layers is therefore desirable.

An encapsulation architecture utilizing a Russian Doll architecture (separating pairs of free-standing barrier films and epoxy seals with nitrogen spacers) (Fig. 5(b)) is introduced to minimize the problem encountered by the nitrogen gas-phase spacer as

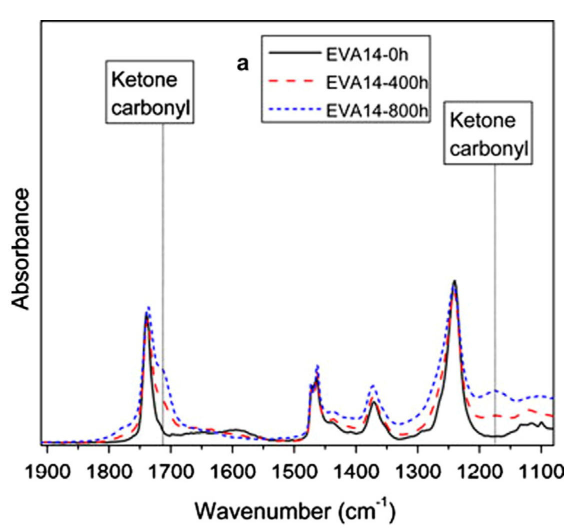


Fig. 4. FTIR spectra of EVA film during UV irradiation [112].

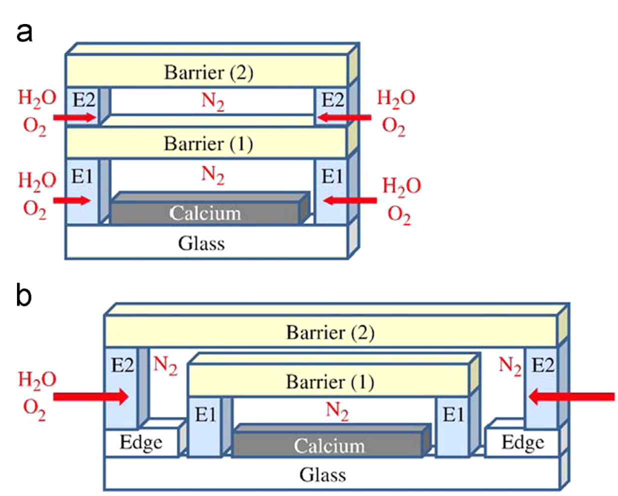


Fig. 5. (a) A calcium film encapsulated with a nitrogen gas-phase spacer between freestanding barrier films and (b) Russian Doll encapsulation architecture [157].

discussed earlier [157]. Unlike the architecture of Fig. 5(a), here permeants have to pass through at least two epoxy layers and a nitrogen spacer permeant sink to reach a device. The calcium thin film optical transmission test indicates that this encapsulating structure results in less than 10% calcium degradation after 95,000 min and a WVTR value of 0.00021 g m^{-2} day^{-1}, confirming that this architecture can enable construction of high performance barriers from low-cost materials [157].

5.2.1.3. Tantalum–silicon–oxygen (Ta–Si–O) and tantalum–silicon–nitride (Ta–Si–N). With a view to establishing a highly efficient barrier against humidity diffusion, thin films of Ta–Si–O/Ta–Si–N were investigated [158]. Investigations show that a 10 nm thick Ta–Si–N layer deposited onto a Ta–Si–O layer reduces CIS solar cell degradation at an accelerated aging test. Transparency is found for Ta–Si–O films over the whole CIS absorption region [158]. With increasing reactive gas content, the deposited films become more and more resistive. At the point of target poisoning, the thin-film resistance is changed from an ohmic to an insulating behavior. The electrical breakdown of 200 nm thick Ta–Si–O films appears at 6.5 MV/cm and reactively sputtered SiO_2 layers break down at approximately 10 MV/cm. Therefore, Ta–Si–O is a good isolator and passes the electrical needs for front diffusion barriers [158]. Reactively sputtered Ta–Si–N films are unstable even under low electrical stress. The thin-film capacitor with a Ta–Si–N dielectric layer reaches no significant breakdown voltage. The weak field stability of Ta–Si–N makes it suitable for using as an additional isolation layer. Altogether, a double-layer encapsulation, consisting of Ta–Si–O and Ta–Si–N, is able to protect a cell well against degradation in the accelerated aging test. Therefore, such a diffusion barrier is a good option for encapsulation of flexible solar modules [158].

5.2.1.4. Al_2O_3/SiO_2. Single Al_2O_3 atomic layer deposition (ALD) films on polymers have demonstrated excellent gas diffusion barrier properties [85,103,104,109]. Further improvements can be achieved using multilayers of Al_2O_3 layers with other inorganic layers [107]. Al_2O_3/SiO_2 bilayers (26 nm and 60 nm, respectively) can reduce the effective WVTR to 1×10^{-4} g m^{-2} day^{-1}, as opposed to $\sim 1 \times 10^{-3}$ g m^{-2} day^{-1} for the 26 nm thick Al_2O_3 layer [107]. Some corrosion of Al_2O_3 layer was reported due to H_2O, which deteriorates the barrier functionality [106]. By the concept of Al_2O_3/SiO_2 bilayers, it is possible to reduce this corrosion substantially and improve the gas diffusion barrier performance [107].

5.2.1.5. Al_2O_3/ZrO_2. Nanolaminate films of Al_2O_3/ZrO_2 thin layers have been investigated to counter the drawbacks of Al_2O_3/SiO_2 bilayers [46,159–161]. Nanolaminates are composite films composed of alternating layers of different materials that often imparts unique properties to the films, which have physical properties that are superior to those of the constituent materials [46]. In this structure, amorphous Al_2O_3 sublayers serve as "termination" layers that hinder the formation of extended ZrO_2 crystallites and the ZrO_2 layer is intended to stop the accumulation of unreacted Al–OH species [159]. The denser $ZrAl_xO_y$–aluminate phase that forms at the interfaces of the nanolaminate layer seems to hinder the penetration of moisture through the layer [46]. Experimental results prove that 100 nm and 130 nm thick Al_2O_3/ZrO_2 nanolaminates achieve permeation rates for both water and oxygen that are about one-half and one-fifth the values for 100 nm and 130 nm thick Al_2O_3 layers, respectively [159]. A WVTR of 2×10^{-4} g m^{-2} day^{-1} is found for a 30 nm thick moisture barrier with this structure at ambient conditions [46]. The permeation rate is determined to be 1.6×10^{-2} cm^3 m^{-2} day^{-1} for oxygen (OTR) under a controlled environment of 70% humidity and 70 °C [159]. Due to these very low permeation rates and the low process temperature, the Al_2O_3/ZrO_2 nanolaminate is able to provide encapsulation for OPV devices [159].

5.2.2. Organic–inorganic hybrid materials

5.2.2.1. Nanocomposite IV. To increase the gas barrier performances of polymer matrices, fillers (e.g. silica, metal oxide, clay, etc.) are added into them [162–166]. However, gas permeation continues for polymer matrices/fillers and metal alloys are therefore been blended with them to reduce the gas penetration [167]. This lab-made nanocomposite IV is applied for the encapsulation of OPV cells.

Thermal characterization reveals that nanocomposite IV has excellent thermal stability since it has a decomposition temperature larger than 300 °C [167]. This is very crucial for the encapsulation of OPV because it can sustain high temperatures and defy the penetration of gas despite the OPV devices liberate much heat when actuated. It also exhibits good gas resistance.

Photoelectric conversion properties and efficiency of 0.42% are found initially in OPV cells without encapsulation [167]. The photoelectric conversion capabilities gradually decay while the actuating time proceeds. This decay is due to the invasion of atmospheric moisture and oxygen into the device, causing corrosion of organic materials and the metal electrode. After being actuated for 48 h, the efficiency reaches 0.016% (decay ratio = 96.2%) [167]. With the encapsulation of nanocomposite IV, the decay ratio is 13.0% and 37.0% when the actuating times are 15 and 48 h, respectively. Along with aforementioned properties, it also has moderate adhesion strength, low shrinkage and fast curing speed that demonstrate the capability of defying the permeation of oxygen as well as moisture of the air into the device, effectively elongating the lifetime of OPV cells [167].

5.2.2.2. SiO_x and organosilicon. Alternating SiO_x and organosilicon layers deposited by PECVD on a poly(ethylene naphthalate) (PEN) substrate are introduced for encapsulation to prolong the lifetime of OPV cells to a greater extent than the organic/inorganic hybrid nanocomposite IV does [168]. SiO_x is produced from a volatile organosilicon precursor under oxidative plasma conditions and organosilicon is deposited using similar organosilicon in a non-oxidizing plasma. The final ultra-high barrier consists of five layers, each approximately 100 nm thick, resulting in a total thickness of 500 nm [168]. This coating is transparent having an optical transmission $T > 85\%$ over the entire visible spectrum. It also shows good resistance to common organic solvents. In the case of encapsulated OPV cells based on MDMO-PPV devices, V_{OC} remains at about 90% of its initial value after 3000 h, as does FF [168].

The 3000 h of device stability achieved by applying encapsulation structure of alternating SiO_x and organosilicon layers is not sufficient for OPV. Developing ultra-high barrier performance encapsulation layer as well as more stable materials for OPV devices is therefore important to extend the cell's lifetime [168]. With a view to this, organosilicon/SiO_x structure is deposited onto the polyethylene terephthalate (PET) substrate by PECVD process [169]. A WVTR of 0.22 g m^{-2} day^{-1} is found for the assembly. By coating 6-pairs of the multilayered structure onto PET, an ultra low WVTR much lower than the MOCON detection limit ($< 1 \times 10^{-2}$ g m^{-2} day^{-1}) is achieved. Such a simple and controllable encapsulation approach is a promising candidate for OPV [169].

5.2.2.3. SiN_x/Parylene. A benefit of SiN_x over oxide or oxynitride as an effective, transparent inorganic barrier coating material is that it does not require reactive oxygen atoms in the deposition process, which could react with the substrate [150]. The OTR and

WVTR decrease as much as thousand fold when the coating thickness of SiN_x exceeds 70 nm. An external tensile state of stress in the SiN_x coating may cause the formation of cracks and the cracked film may also debond from the substrate along the interface. One way to further improve the barrier performance is to deposit a smoothing, defect decoupling organic film on top of the inorganic layer. With a view to this SiN_x/Parylene multilayered structure is introduced [150]. It results in an improved permeation resistance of the coating as well as an improved resistance to crack formation. After 3000 times cyclic bending, the WVTR and OTR of the two pairs of Parylene/SiN_x coatings can be maintained at a level near 0.01 g m^{-2} day^{-1} and 0.1 cm^3 m^{-2} day^{-1}, respectively. The barriers exhibit moisture and oxygen barrier performance below the detection limit of the MOCON instruments [150]. SiN_x/Parylene is therefore a good candidate for the encapsulation of OPV [150].

5.2.2.4. SiO_x/SiN_x/Parylene. Inorganic encapsulation films show limited barrier performance due to microdefects [170]. These defects provide easy pathways for moisture and oxygen diffusion, and thus limit the barrier characteristics [171]. The microdefects can easily promulgate to form cracks, which render such flexible films permeable. An organic barrier film with the low internal stress, high transparency, and pinhole-free can be used to suppress the crack elongation. A multilayer encapsulation structure composed of SiO_x, SiN_x and Parylene is therefore investigated for permeation barrier applications [151,171]. After 75 days, the WVTR can reach 2.5×10^{-7} g m^{-2} day^{-1}, as calculated by the calcium test [151]. After being flexed for 5000 times, the WVTR value almost keeps around 2.1×10^{-6} g m^{-2} day^{-1}. Therefore, the performance of this multilayer barrier structure has a high potential for OPV [171].

5.2.3. Comparison of multilayer encapsulation films

Russian doll architecture minimizes the problem of diffusion through epoxy layers [157]. However, desired lifetime is not achieved by this approach. Multilayer structure of Ta–Si–O and Ta–Si–N is an improvement over Russian doll architecture. These films have an amorphous-like microstructure although they both are grown on crystalline substrates. Ta–N films without silicon are slightly crystalline. Tantalum-oxygen films deposited on native silicon-oxide also grow amorphous-like. In the case of a polycrystalline substrate, the microstructure is reproduced from the substrate so that the Ta–O microstructure becomes polycrystalline. The grain boundaries in polycrystalline films are fast diffusion paths for humidity resulting in a significant decrease of the PV cell efficiency. Al_2O_3/SiO_2 films show better efficacy in that sense. However, the deposition temperature needed is 175 °C, whereas a temperature below 100 °C is required for deposition on top of OPV devices [107]. Moreover, larger thicknesses and greater brittleness may cause cracks under the strain of handling and mounting the ALD-coated polymer films. Al_2O_3/ZrO_2, nanocomposite IV and UHB coating are other encapsulants used to solve the encapsulation problems. However, none of them meets the desired lifetime criteria.

6. Summary of encapsulating materials

Permeation of about two to three orders of magnitude lower than the bare substrate is usually considered satisfactory to ensure encapsulation requirements (Table 1). It has been shown that the best transparent single-layer barrier performance is achieved for silicon-based dielectric films deposited by PECVD [88]. However, single layer barriers cannot reach permeation levels lower than 1000 times that of bare polymer substrates. Increasing the thickness of a single-layer barrier leads to a non-zero asymptotic value of OTR that is controlled by the number of defects present in the barrier layer. These defects are mainly caused by intrinsic or extrinsic surface roughness [172]. Hence, these nanometer size structural defects account for the limited performance of single-layer gas barriers. Besides, theoretical calculations have shown that the total permeation rate through many small pinholes is much higher than that corresponding to the same total pinhole area combined in a few larger defects [173]. This can be explained by lateral diffusion, and it is of crucial importance when the diameters of the defects are small compared with the thickness of the substrate. It has been proven that deposition of multilayered inorganic films generally improves the barrier performance only slightly. The most common technique used to achieve high performance barriers is based on organic–inorganic multilayers. However, several constraints on the development and utilization of thin-film encapsulation technologies exist that make their development challenging. A variety of materials have been developed to face these challenges that improve lifetimes and one notable case is titanium oxide (TiO_x). It cannot satisfy the encapsulation requirements of organic devices, however, results prove the concept of using thin films as barriers to encapsulate devices. The simplest example of encapsulation is the use of glass plates. This provides the level of oxygen protection required by the industry, however, glass creates inflexible devices. Research also

Table 2
Summary of encapsulating materials.

Material	Encapsulation type	WVTR (g m^{-2} day^{-1})	Comment	Reference
SiN_x	Single layer (inorganic)	< 0.01	Passivation properties should be improved	[96]
Al_2O_3	Single layer (inorganic)	1.7×10^{-5}	Permeation governed by nanoscale defects	[103]
PVB	Single layer (organic)	50 (at 38 °C/100% RH)	Time consuming vacuum lamination Low mechanical strength	[174]
ORMOCER®	Single layer (organic–inorganic hybrid)	0.01	Surface roughness Biological disadvantages	[125]
SiO_x/SiN_x	Multilayer (inorganic)	3.12×10^{-6}	High deposition temperature	[152]
N_2 gas phase spacer	Multilayer (inorganic)	2.1×10^{-4}	Lifetime expectancy	[157]
Al_2O_3/SiO_2	Multilayer (inorganic)	1×10^{-4}	High deposition temperature (175 °C) Formation of cracks	[107]
Al_2O_3/ZrO_2	Multilayer (inorganic)	2×10^{-4}	Lifetime expectancy	[46]
Organosilicon/SiO_x	Multilayer (organic–inorganic hybrid)	22×10^{-2}	Formation of defects Degradation of reliability due to residual compressive stress	[169]
SiN_x/Parylene	Multilayer (organic-inorganic hybrid)	1×10^{-2}	Poor adhesion between organic and inorganic layer Durability is dependent on coating thickness	[150]
SiO_x/SiN_x/Parylene	Multilayer (organic–inorganic hybrid)	2.5×10^{-7}	WVTR is dependent on coating thickness Lifetime expectancy	[151,171]

shows that a layer of SiO_xC_y performs well. Unfortunately, despite being flexible, and resistant to oxygen transmission, this encapsulation must be performed with PECVD process that involves expensive, and complicated vacuum systems. There are many other materials used for the encapsulation purpose, however, in general they cannot fully satisfy the barrier requirements. A review of these materials and methods used for different encapsulation approaches as well as their integration with PV devices have been presented in this paper. Some of these materials and methods are summarized below in terms of their WVTR and drawbacks in Table 2.

Recently, linalyl acetate [126,175] and terpinene-4-ol [176] have been used to fabricate thin films using RF plasma polymerization technique. The obtained optical and surface properties of these polymer thin films substantiate the potential of these materials as encapsulating layers for OPV [126,177,178].

7. Conclusions and recommendations

Thin film encapsulation is a critical technology required for the application and commercialization of OPVs. Effective encapsulation to prevent the permeation of water vapor and oxygen, which degrades OPV devices, is key for achieving the reliability and desired lifetimes. The materials applied for this purpose, cannot yet satisfy the encapsulation requirements discussed in this paper. Adhesion strength of EVA is affected by the processing conditions, damp heat and exposure time. The deposition of the SiO_x and SiN_x encapsulation structure causes plasma damage on the devices owing to the high sensitivity of the organic films to radiation, charging and heating. Al_2O_3 has a slow deposition rate compared to PECVD-based methods that makes it more difficult to use in low-cost mass manufacturing processes. Other materials found in the literature could not satisfy the lifetime requirements. The problems of achieving ultrahigh barriers therefore become apparent from these issues, with permeation depending ultimately on transport through local pinholes that are difficult to control and to avoid. Hence, new materials are needed which will satisfy the encapsulation requirements and achieve the reliability and lifetime required. Furthermore, the processing temperature of the thin film encapsulation must be suitable for the temperature range of the organic and polymer substrate materials. Often, inorganic layers processed at low temperature using techniques such as PECVD produces layers that are not perfect barriers due to many intrinsic defects in the films. Water vapor and oxygen therefore diffuse predominantly through these defects that must be reduced or passivated to produce high performance barriers for encapsulation. Multilayer films consisting of alternating inorganic and organic layers can be one solution to this, where the defects in the inorganic layers are interrupted and do not channel continuously through the film structure. However, the barrier performance of the multilayer structures consists of a steady state permeation rate as well as a transient rate that exists over a specified period (lag time) that may be longer than the desired lifetime of the encapsulated OPV devices. In addition, the permeation rate in the transient region is generally lower than the steady-state permeation rate, so characterizing the barrier performance simply from the initial transient period generally yields an underestimation of total permeation rate for long-term applications. As a result, characterization of the barrier performance in multilayer structures should separate the permeation rates in terms of the steady-state and transient regions and account for the lag time in order to prevent overestimation of barrier performance or expected device lifetimes during long-term storage or application. Furthermore, high quality inorganic layer deposition with vacuum deposition processes is an expensive and low throughput method. Multilayer barrier structures obtained with vacuum deposition process are therefore often expensive due to the alternate deposition of organic and inorganic layers in different deposition chambers. Solution precursors for inorganic layers can be a promising alternative where it may be possible to deposit organic/inorganic structures with a same deposition process and with a high throughput. Hence, a promising way to obtain low cost barrier materials for OPV encapsulation is the realization of high barrier materials with a totally liquid process.

Optimizing the dimension of individual films or replacing some of the constituent films with others deposited by different processes can be considered as an alternative based on the encapsulation structures discussed in this paper. Further study for reducing processing time and steps is required. Efforts to improve the quality of films should also be addressed before adapting these technologies. In addition to reducing processing steps and time, studies concerning the reliable and continuous yield of encapsulation processes should be performed. In summary, high quality encapsulation layers are critical for improving the life span of OPV devices, and further research is needed to improve the quality of materials suitable for encapsulation layers.

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